attenuated sources as the nebulæ might reasonably be expected to be concentrated near the limit of the series. In the absence of any theory or experimental data which would give a clue to the energy distribution from a source of infinite attenuation, even an approximate estimate of the probable relative intensities of the higher members under the conditions of our experiments is impossible, but, from the available evidence, we feel justified in concluding that assumptions of a far-reaching character will be needed to explain our results in the light of Bohr's theory. We can at present offer no explanation for the phenomena observed; we fear that they constitute a fresh difficulty of some importance in the construction of any theory of the genesis of spectra.

Researches on the Chemistry of Coal. Part I.—The Action of Pyridine upon the Coal Substance.

By WILLIAM A. BONE, D.Sc., F.R.S., and REGINALD J. SARJANT, M.Sc.

Introduction.

The experiments recorded in this paper are part of a research carried out in the Department of Chemical Technology at the Imperial College of Science and Technology, at the instance of the British Association Fuel Economy Committee, with the double object of clearing up certain discrepancies in the work of previous investigators and of gaining further knowledge of the chief types of constituents contained in the coal substance.

One of the authors having recently reviewed at some length the present state of science with regard to the composition of coal in his monograph on "Coal and its Scientific Uses" (pp. 35 to 163 inclusive) there is no need to treat of the matter again at any great length here. Special attention may, however, be drawn to the summarised statements given on pp. 111 to 112 and 124 to 128 (inclusive) of that monograph concerning the results and views of previous workers and the present state of our knowledge with regard to the primary action of heat upon coal.

There is now general agreement amongst chemists that the constituents of the coal substance may be regarded as consisting principally of three distinct types derived respectively from the ligno-celluloses, resins, and proteins contained in the vegetable *débris* from which the coal originated.

These bodies have, during the formation of coal, been subjected first of all to the disintegrating influence of decay and bacterial action, as in modern peat bogs, followed by the combined action, continued through long geological ages, of great pressure and a slowly rising temperature, which latter, however, has probably not exceeded 300° C. and may have been considerably less. In these circumstances, the relatively unstable cellulosic and proteid constituents would probably undergo such profound changes as would to a great extent mask their original characters, whilst it might be expected that the more stable resinous constituents would be effected to a considerably less degree.

Hitherto it has not been found possible to devise an experimental method for separating the three types of constituents sufficiently well to permit of more than a partial delineation of their chemical behaviours being made. Strangely enough, also, some investigators have spoken of the coal substance as though it contained only cellulosic and resinic derivatives, ignoring the equally important nitrogenous constituents.

Amongst the methods chiefly employed for separating the said constituents, perhaps the most important has been the action of various solvents, and particularly of pyridine, picoline, quinoline, and aniline, upon the coal substance.

Bedson (in 1899) was the first to draw attention, in a paper before the North of England Institution of Mining Engineers, to the remarkable solvent action of pyridine upon bituminous coals, and subsequently, in 1908, he described the details of his work in this connection in a paper read before the Newcastle-on-Tyne Section of the Society of Chemical Industry.[*] Since that time the method has been extensively employed by other investigators chiefly by R. V. Wheeler and his co-workers,[†] and also by Wahl[‡], and Harger.[§] Vignon[||] has similarly investigated the solvent action of aniline and quinoline upon the coal substance.

Clark and Wheeler (*loc. cit.*) have claimed that if the solvent action of pyridine is supplemented by a subsequent chloroform extraction of the original pyridine extract, a complete separation of the resinic from the cellulosic constituents may be effected. But a critical examination of the analytical data published in their paper leaves some doubt in the mind as to the validity of this conclusion, although doubtless a partial separation can be so effected. Their experimental results also show that there had been some

[*] 'Journ. Soc. Chem. Ind.,' p. 147 (1908).

[†] Burgess and Wheeler, 'Trans. Chem. Soc.,' vol. 99, p. 649 (1911); Clark and Wheeler, *ibid.,* vol. 103, p. 1704 (1913).

[‡] 'Compt. Rend.,' vol. 154, p. 1094 (1912).

[§] 'Journ. Soc. Chem. Ind.,' p. 389 (1914).

[||] 'Compt. Rend.,' vol. 158, p. 1421 (1914).

absorption of oxygen by the material during the extraction processes and, in our opinion, these authors did not sufficiently take into account the nitrogenous constituents of the coal substance in applying their method.

The subsequent independent investigations of Harger, Wahl, Vignon, and others have raised the question as to whether the action of pyridine, and other similar basic solvents, is really a case of ordinary solution, for much of the evidence suggests that it is essentially a depolymerising one. Our own work on the subject supports the view recently put forward by one of us that " besides any ordinary solvent action which pyridine may have upon the resinic constituents, which is probably fairly rapid, it also at the same time slowly attacks and resolves into simpler molecular aggregates the complex structure of the coal substance as a whole."*

In extracting a coal with pyridine in a Soxhlet apparatus in the manner first described by Bedson, and afterwards (with slight modification) by Wheeler and his co-workers, irregularities are frequently encountered, both in regard to speed and ultimate extent of the solvent action. So marked were these found to be in the cases of certain coals examined that the authors determined to subject the action of pyridine to a close examination, with a view to determining the causes of such irregularities.

Experimental.

In an extended series of preliminary experiments, the results of which need not here be detailed, it was found:—

(1) That the presence of oxygen has an important retarding action, varying considerably with the nature of the coal, upon the extraction process. This is due to the fact that the coal substance, and any pyridine solutions obtained therefrom, absorb oxygen and undergo oxidation during the extraction process. Also, it was found that the previous "oxygenation" of the coal substance renders it much less susceptible to the solvent action of pyridine. Therefore, in order to obtain comparable results with various coals, it is necessary to exclude access of oxygen during the extraction process, which is best carried out in an inert atmosphere.

(2) That the presence of water in the pyridine used has a strong retarding influence upon its solvent action. On the other hand, the presence of picoline and higher homologues of pyridine affect the solvent action but are less stable. Hence the pyridine should be carefully purified and dehydrated before use, or otherwise discordant results as between various coals may be obtained.

* 'Coal and its Scientific Uses,' p. 93.

(3) That the degree of fineness of the coal operated upon must also be taken into consideration. The coal itself should be carefully dried beforehand, and then ground until it passes through a standard mesh. This, however, should not be too fine, because after a certain limit of fineness has been passed there is a tendency for the finest particles to be carried over mechanically into the flask of the extraction apparatus during the periodic siphoning. Thus, for example, we have found that in most cases the best results are obtained when the dried sample has been ground so as to pass through a standard mesh of 90 to the linear inch.

(4) It is also preferable, though not essential, to arrange the conditions so as to ensure, as far as possible, equality of temperature in the extraction chamber of the apparatus, and also to maintain a regularity in the rate of siphoning during the extraction process. Hence it is desirable to employ some uniform or standard size of extraction chamber and to lag it efficiently. Also, to have all the temperature conditions well under control, and especially the rate of vaporisation of the solvent.

We will now describe the methods and apparatus employed by us to meet the foregoing requirements.

Purification of the Solvent.

Commercial pyridine always contains picolines and lutidines, and it also has a strong affinity for water forming hydrates, principally $C_5H_5N, 3H_2O$ (b.p. 95° C.). That supplied to our laboratory was found to contain only about 40 per cent. of basic substances, the remainder being principally water.

After investigating a number of possible methods of separating the pyridine from its various homologues (such as, for example, by means of their hydrochlorides, zinkichlorides, or their compounds with potassium ferricyanide), all of them were finally abandoned in favour of oxidising these impurities by means of a mixture of nitric and chromic acids.

To 900 c.c. of the crude liquid were added 50 grm. of chromic acid and 100 c.c. of nitric acid, and the mixture was then heated in a reflux apparatus for 18 hours. To the cooled liquid 70 grm. of sodium hydroxide were cautiously added. Care was taken not to allow the liquid to become too hot during these operations, for otherwise a point of sudden decomposition would have been reached involving loss of material and some risk of fire.

The liquid was thereupon filtered and afterwards fractionally distilled. Each fraction was dehydrated by the action of quicklime or sodium hydroxide in the first place, and subsequently by prolonged contact with solid caustic potash. After dehydration the fractions were re-distilled under reduced

pressure, moisture being carefully excluded from the apparatus. Only those fractions boiling at atmospheric pressure between 115° and 117° C. were employed for the subsequent extraction operations.

The purity of the solvent so obtained was always carefully checked by density determinations. Thus, for example :—

Boiling point of fraction.	Density referred to water at 4° C.	Temperature.
° C. 115–116 115–117	0·9855 0·9850	° C. 15·2 13·1

According to Perkin, the density of pure pyridine (b.p. 115·2° C.) referred to water at 4° C. is 0·9855.

Preparation of the Coal Samples.

The coal was first of all ground so as to pass a mesh of 90 to the linear inch, and then dried in a thin layer in an exhausted desiccator over either concentrated sulphuric acid or phosphoric anhydride. The upper part of the desiccator was fitted with a small electric heater, the radiation from which enabled the temperature of the coal to be raised up to between 80° and 95° C. This greatly accelerated the drying operations without alteration of the coal substance. On the whole, phosphoric anhydride was found to be a more satisfactory drying agent than the sulphuric acid.

The Extraction Apparatus.

The devising of a satisfactory form of Soxhlet apparatus for the extraction of coal by such solvents as pyridine in an inert atmosphere without inleakage of air was not altogether an easy problem. The chief difficulty encountered was the tendency of pyridine vapour to penetrate in time through even the best ground glass joints that could be made between the evaporation flask and the extraction chamber. And any such escape of pyridine invariably involved a considerable loss of solvent and an inleakage of air at that joint. Finally, it was found necessary to substitute a fused glass joint, which involved making the whole apparatus from the extraction chamber downwards in one piece. No difficulty, however, was encountered in preventing air leakage through a ground glass joint between the extraction chamber and the water-cooled condenser of the apparatus. The final form of apparatus and its connections is shown in the accompanying diagram (fig. 1). The evaporation flask had an external diameter of 9·5 cm., and a capacity of

To Extraction Apparatus

To Gas Cylinder

Rubber Pressure Tubing

Two way Tap

Soft Rubber Pressure Indicator

To Fleuss Pump

Gasholder

$CaCl_2$

$Ca.O.$

Drying Towers

Fig. 1.

Gas inlet

Condenser

Vapour Tube

Asbestos sheet lagging

Asbestos lagging

Solvent

Thimble

Siphon Tube

Electric Heater

N.S. 1918.

Brass stands with adjustable feet

Movable Asbestos Covers

"Efesca" Electric Firebar Heater

Asbestos
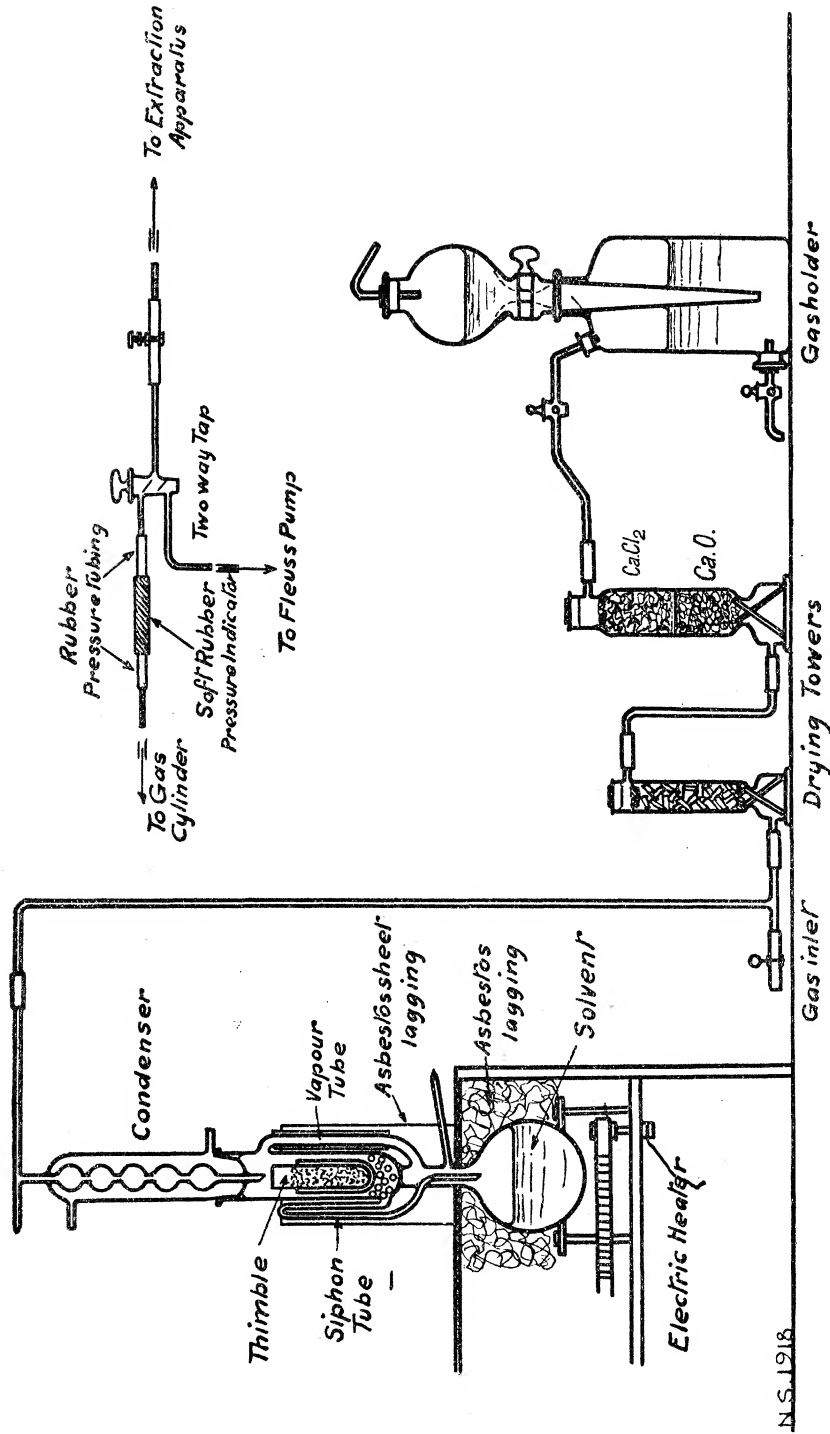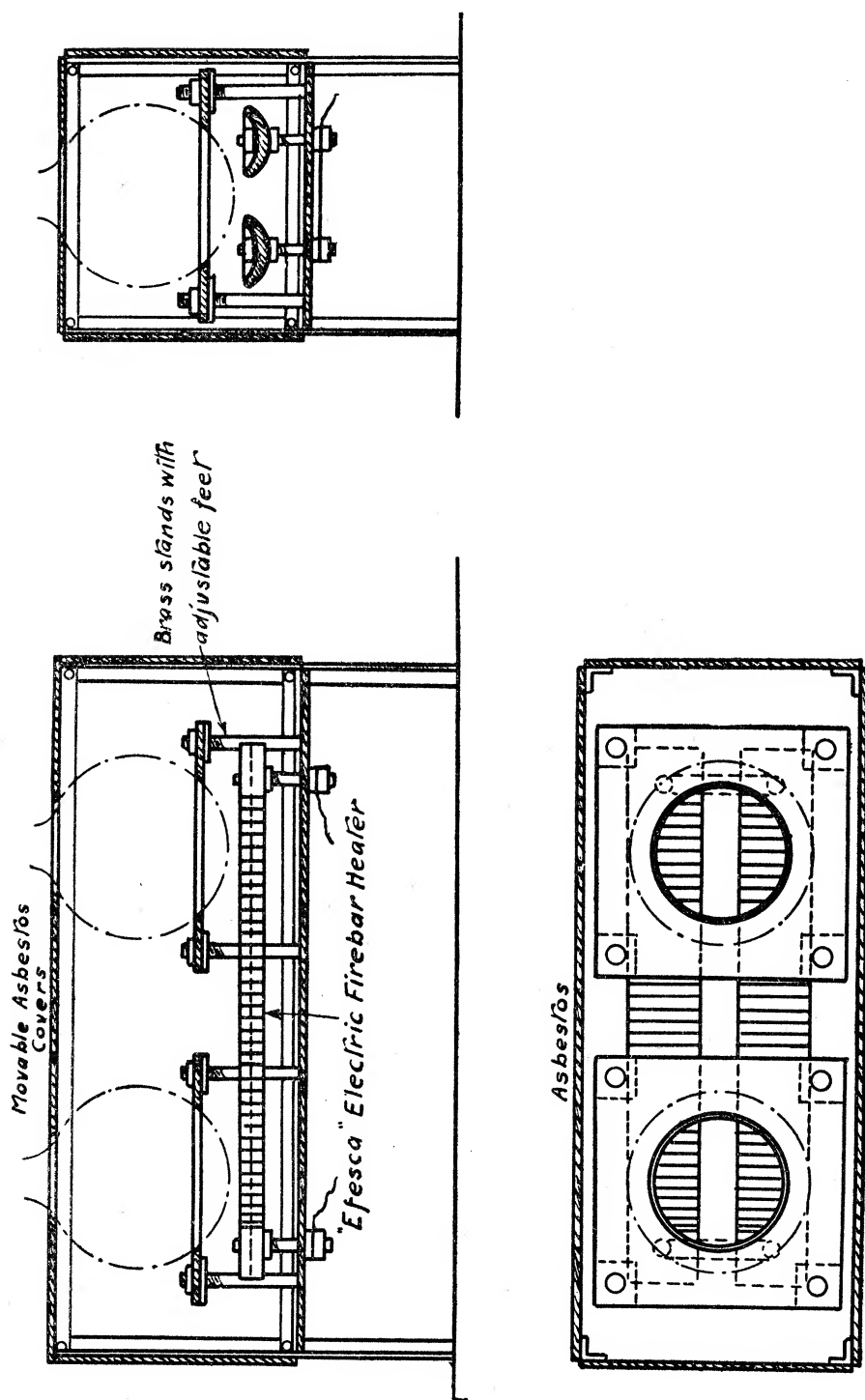
Fig. 2.

approximately 450 c.c. The dimensions of the cylindrical extraction chamber were : Length 20 cm., and external diameter 3·7 cm. The water-cooled condenser (length 22 cm., and external diameter 3·7 cm.) contained five bulbs in series.

At the top of the condenser connection was made through two drying towers in series (one of which, $9'' \times 1\frac{1}{2}''$, contained sticks of solid caustic potash, and the other, $12'' \times 2''$, granulated calcium chloride over lumps of quicklime) to a 2-litre gasholder containing nitrogen over a mixture of equal volumes of glycerine and water.

The extractors were mounted in pairs on an electric heater. Each heater (fig. 2) consisted of a rectangular box of asbestos board screwed on to a
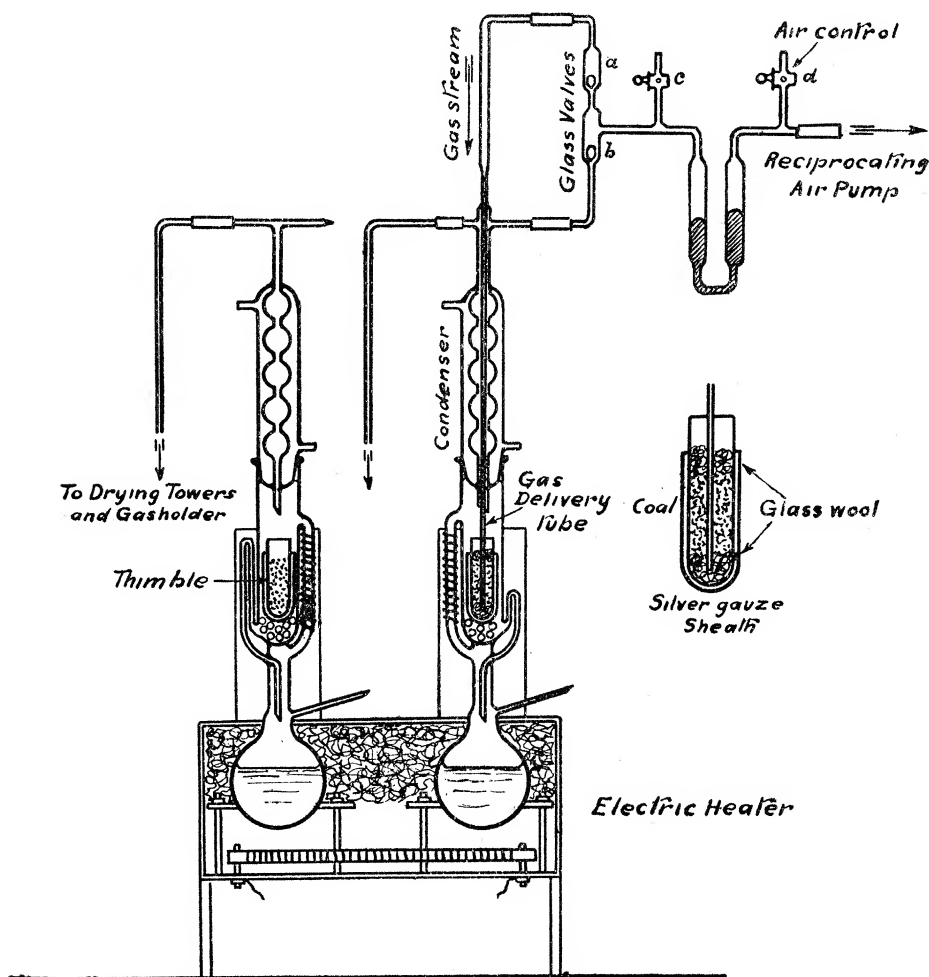

Fig. 3.

framework of angle iron. Two ribbon-wound bar heaters of fireclay, wired for use either in series or in parallel, were placed side by side at the bottom. The flasks of the extractors were supported on brass frames covered with asbestos. The space between the flasks and the sides of the heater was lagged with asbestos wool, the extraction chamber being protected with shaped screens of asbestos board. The arrangement finally adopted of two extraction apparatuses, mounted for parallel experiments in atmospheres of (i) nitrogen and (ii) "moving" oxygen, is shown in fig. 3.

Method of Extraction.

About 10 grm. of the dried coal was weighed out into a dry paper or alundum thimble.* The extractor flask was then filled with a measured volume of the pure dry solvent, the thimble placed in the extraction chamber, and the apparatus assembled, a small quantity of lubricant being used to make the ground glass joint tight. The apparatus was then evacuated with the Fleuss vacuum pump, and nitrogen allowed to enter slowly from a cylinder through a reducing valve.† This operation of evacuation and filling was repeated three times, and then the taps on the gasholders were opened to put the extractor in communication with the gas in the holders. Gas samples were then taken and analysed, and if the oxygen present did not exceed 0·5 per cent. the extraction was started. Gas analyses were also made at the end of each operation.

Removal of the Solvent.

In the subsequent recovery of the extract, the solution was rapidly filtered through a Buchner funnel; the flask was washed out with hot solvent, which, being passed through the filter, served also to dissolve any extract precipitated on cooling. Filtrations through a Gooch crucible were carried out in a jacketed arrangement, which enabled the operation to be done in an atmosphere of nitrogen.

The clear liquid was thereupon concentrated by distillation under reduced pressure. Most of the remaining solvent was removed by alternately heating the residue in the flask from 50° to 60° C. in an atmosphere of nitrogen and evacuating until of constant weight. It was found, however, that this

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* The use of a paper thimble is usually to be preferred, as it ensures a more rapid extraction; the tendency of the paper to break open during a prolonged experiment may be counteracted by strengthening the thimble with a silver gauge sheath, as shown in fig. 3.

† The connections used for these operations are shown in the upper right-hand portion of fig. 1.

treatment failed to remove all the pyridine, and in all our later experiments the concentrated extract was poured into an excess of hydrochloric acid, and was finally collected by filtration through a weighed Gooch crucible, washed, and dried *in vacuo* over strong sulphuric acid.

The insoluble residue in the thimble of extraction chamber was collected, and, after being washed with dry ether, was kept *in vacuo* over strong sulphuric acid with the object of removing any "absorbed" pyridine. But, as will be explained later, so tenaciously was the latter retained, that further special treatment had to be resorted to, before it could all be finally eliminated.

Types of Coal Used.

Our experiments have so far been principally confined to two typical bituminous coals, namely, (i) a Durham "coking" coal, A., and (ii) a Barnsley "hard steam" coal, B., which were selected as having nearly the same percentage compositions, notwithstanding considerable differences in their other properties. Their ultimate compositions were as follows :—

	C.	H.	N.	S.	O.	Ash.
	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
A. Durham coking coal	83·73	4·76	1·09	1·28	7·52	1·62
B. Barnsley hard steam coal	82·33	4·99	1·50	0·70	7·72	2·76

These coals behave quite differently on carbonisation at 950° C. The coal A. intumesces and swells considerably, yielding 26·3 per cent. of volatile matter and a residue of very hard "metallurgical" coke. Coal B., on the other hand, does not swell or go through a stage of intumescence, but yields 32·2 per cent. of volatile matter and a much weaker coke. Moreover, when both were exposed to the action of oxygen at a constant temperature of about 108°, the Barnsley coal absorbed the oxygen more quickly than did the other.

In this connection, it may be stated that a comparative study of the behaviour of the two coals, when separately carbonised at a temperature of 550° C., indicated that B. was relatively richer in cellulosic constituents than was A.

Part I.—EXPERIMENTS WITH COAL A.

(1) *Comparison between the Action of Pyridine and Picolines.*

The object of these experiments was to determine whether or not, on extraction under ordinary pressure in the Soxhlet apparatus,—

(*a*) There is a limit to the solvent action of pyridine or picolines on the coal substance ; and

(*b*) There is any difference in either the rate of solvent action, or ultimate proportion of the constituents extracted, by pyridine and picolines respectively.

The pyridine employed was a fraction of the purified anhydrous solvent, boiling between 115·3° and 116·3°, whilst the picolines were a fraction of anhydrous pyridine homologues boiling between 130° and 150°. For this purpose the dried coal was continuously extracted in an atmosphere of nitrogen, in the first instance for an uninterrupted period of 159 hours, after which the residue was similarly extracted for a further period of 24 hours.

Experiment.	Solvent.	Percentage of dry coal extracted in	
		159 hours.	183 hours.
A. 1	Pyridine	31·84	32·27
A. 2	Picolines	30·26	31·20

The above figures show that the amount extracted in the two cases approached the same practical limit, which, it should be noted, exceeds considerably the amount of volatile matter expelled from the coal at 950°. There was nothing to show that the picolines acted more quickly than pyridine upon the coal substance ; indeed, owing to the lesser stability of the picolines, pyridine appeared to be the better solvent generally.

The "residues" were subsequently extracted with dry ether to remove any mechanically-held solvent, and afterwards kept in a vacuum over sulphuric acid for 48 hours. After such treatment their weights were 72·3 and 73·2 per cent. respectively of the original dry coal, from which already 32·2 and 31·2 per cent. of material had been extracted by the solvent. The explanation of this is that the coal substance has a marked affinity for the basic solvents employed, the actions of which are not merely those of ordinary solvents, but partake of a chemical character. The best way of removing from such residues the proportions of "combined" pyridine, etc., which they so obstinately retain, is to wash them first with dilute hydrochloric acid and then with ether.

Character of the " Extracts " and " Residues."

The "extracts" so obtained were resinous powders of dull chocolate brown colour. The "residues" were very hygroscopic powders, dull black in colour.

On carbonisation, the "extracts" passed through a definite stage of intumescence, leaving a very swollen and puffy coke. The "residues," on the other hand, passed through no such stage of intumescence, the carbonised remainder possessing hardly any cohesiveness.

(2) *The Retarding Influence of Oxygen upon the Extraction Process. Parallel Extraction in* (i) *Nitrogen and* (ii) *Oxygen.*

The next experiments show how greatly the extraction process with this coal was retarded by the presence of oxygen. In two parallel experiments, carried out simultaneously and under precisely the same conditions, the dry coal was extracted in an atmosphere of (i) nitrogen and (ii) oxygen for a definite time period until the solvent action appeared to have almost ceased in the first-named case. In one pair of experiments the oxygen was continuously circulated in the Soxhlet apparatus by means of a special mercury pump operated by an electric motor and an air-pump (fig. 3). In the other pair of experiments no such artificial movement was imparted to the atmosphere. Seeing that each apparatus was throughout an experiment in free connection with the gasholder containing the nitrogen or oxygen, as the case might be, the gaseous pressure would be kept constant, and any oxygen absorbed would at once be automatically replaced.

As a rule, visible solvent action had almost ceased after about four days, although the experiments were kept on much longer, so as to allow ample time for a practical limit to be reached in each case. In the "oxygen" experiment about 80 c.c. of the gas (equivalent to about 1 per cent. of the weight of the coal substance used) were absorbed during the first four days, and some further absorption occurred during the remainder of the experiments. The following results of two pairs of parallel experiments may be quoted as typical :—

Experiments A. 3 and A. 4.   Coal ground to pass mesh 90.
Total Period of Extraction = 11 days $7\frac{1}{2}$ hours.

Experiment.	Atmosphere.	Percentage extracted.
A. 3	Nitrogen	29 ·72
A. 4	Moving oxygen ...	17 ·03

Experiments A. 9 and A. 10.   Coal ground to pass 150 mesh, but not 200.
Total Period of Extraction = 7 days 2½ hours.

Experiment.	Atmosphere.	Percentage extracted.
A. 9	Nitrogen	32·48
A. 10	Oxygen	17·75

In addition to the proof thus given of the marked retarding effect of oxygen upon the extraction process, there was also clear evidence of a definite " affinity " of the coal substance, and particularly of the " residue " left in each case, for pyridine. Thus, for example, in the case of A. 9, the " residue," after being washed with dry ether and subsequently kept *in vacuo* over strong sulphuric acid for 23 days, weighed 77·33 per cent. of the original coal substance, although no less than 28·86 per cent. of the latter had been extracted in a first treatment. In the case of A. 10 the " residue " weighed as much as 92·75 per cent. of the original coal treated, although 16·23 per cent. of the latter had been extracted.

(3) *Practical Limit of Pyridine Extraction and Proportion of Extract soluble in Chloroform.*

From the four following experiments, in which the coal was extracted with pyridine in an atmosphere of nitrogen until the process had reached its practical limit, it would appear that the extractable matter amounted to somewhere between 30 and 33 per cent. of the weight of the dry coal, thus :—

	Experiments.				Mean.
	A. 1.	A. 2.	A. 9.	A. 13.	
Percentage extracted	32·27	31·20	32·48	30·44	31·60

A composite sample of such extracts was subsequently extracted in the Soxhlet apparatus with chloroform in an atmosphere of nitrogen for a period of two days, when approximately 52 per cent. of its weight was dissolved. The resulting " chloroform " extract certainly contained both nitrogen and sulphur, and could not be regarded as a pure resinous substance, although it was undoubtedly for the most part resinous in character, as was also shown by its action upon a photographic plate at a temperature of 45° to 55°.

The following analytical results show that, whilst the composition of the "residue" left after the pyridine extraction is far removed from that of any "resin" hitherto found in, or associated with, coal (such resins usually contain upwards of 8·0 per cent. of both hydrogen and of oxygen), that of the pyridine-chloroform "extract" (*c*) does not sufficiently agree with the same to warrant the view that it represents even a nearly pure coal-resin. A method (discovered during the course of another cognate research at the Imperial College) for isolating pure resins from the coal substance will be described in a later communication.

	Percentage composition.						Ratio C/H.
	C.	H.	S.	N.	O.	Ash.	
(*a*) Original coal	83·73	4·76	1·28	1·09	7·52	1·62	17·60
(*b*) "Residue" after pyridine extraction	84·14	4·40	0·93	1·86	4·53	4·14	19·12
(*c*) Pyridine-chloroform "extract"	80·09	5·96	13·95			—	13·44

(4) *Character of the Prolonged Action of Pyridine.*

In all the pyridine extraction experiments, evidence was forthcoming that the action, whilst it finally approached the aforesaid "practical limit," never ceased altogether. Generally speaking, the solvent action was marked by the appearance of a distinct reddish colour in the liquid around the thimble in the extraction chamber, and its termination was signified by the disappearance of such discoloration. Now we repeatedly observed during the investigation that, after the coloration had entirely ceased, and the extraction had therefore been suspended, it re-appeared whenever the apparatus had been left standing for several days with the solvent still in contact with the "residue" in the thimble in the nitrogen atmosphere. Thereupon, on resuming the extraction process in the usual manner, the colour would again disappear after a few hours, but would once more reappear on further standing. In one experiment the phenomenon of alternate disappearance and reappearance was repeated no less than 11 times during a period of 53 days in which the coal was intermittently extracted for altogether 13 days and 19 hours, and betweenwhiles left in contact with the solvent at the laboratory temperature. This supports the view that the so-called "solvent action" of pyridine upon the coal substance is really a more complex phenomenon than has usually been supposed, involving, in addition to a rapid dissolving of the "resinous" constituents, a simultaneous and much

slower " unbuilding," or depolymerising, of the whole coal structure, which was thus gradually brought into a more soluble condition.

(5) *Action of Pyridine at* 130° *to* 150° C. *under Pressure.*

Confirmation of the foregoing supposition was forthcoming when the coal was subjected to prolonged heating with pyridine at temperatures between 130° and 150° C. in sealed tubes, the air in which had been displaced by nitrogen before sealing. No apparent thermal decomposition, either to the coal or to the solvent, occurred during the operation. After opening the tubes and filtering their contents, the " residues " were repeatedly treated with successive portions of boiling pyridine until no further matter could be so extracted. Finally the " extracts " were removed, washed with dilute hydrochloric acid, and dried. The following results show how greatly the percentage amounts of " extracts " exceeded those previously obtained by the usual Soxhlet method :—

Experiment.	Weight of coal taken.	Volume of solvent used.	Duration of heating in days.	Percentage of dry coal extracted.
	grm.	c.c.		
A. 21	2·01	123	19	57·16
A. 22	2·00	163	26	63·63
A. 23	1·21	129	26	67·63

Part II.—Experiments with Coal B.

The results of the following experiments demand attention because they are so strikingly different from these similarly obtained with the " isomeric " coal A.

(1) *Parallel Extraction in Atmospheres of* (i) *Nitrogen and* (ii) *Oxygen.*

In these experiments, which were carried out in a similar manner to A. 3 and A. 4 (*q.v.*), the dry coal was extracted with pyridine first of all (*a*) for a period of 2 days and 22 hours, after which the solvent was replaced by a fresh portion, and (*b*) the process continued for a further period of 46 days and $17\frac{1}{2}$ hours, with the following results :—

Experiment.	Atmosphere.	Duration.	Percentage extracted.
B. 3.....................	Nitrogen	(*a*) 2 days 22 hours. (*b*) 46 „ $17\frac{1}{2}$ „	$\left.\begin{matrix} 9\cdot12 \\ 2\cdot49 \end{matrix}\right\} = 11\cdot61.$
B. 4.....................	Oxygen	(*a*) 2 „ 22 „ (*b*) 46 „ $17\frac{1}{2}$ „	$\left.\begin{matrix} 7\cdot64 \\ 5\cdot43 \end{matrix}\right\} = 13\cdot07.$

Comparing these results with those of A. 3 and A. 4 respectively, it will be seen that whereas the Durham coking coal ("volatiles" = 26·3 per cent.) yielded (in nitrogen) between 30 and 32 per cent. of "extract," the Barnsley coal ("volatiles" = 32·2 per cent.) yielded only 11·6 per cent. of "extract," a fact which sufficiently proves that there is no necessary relationship between the amount of "volatiles" yielded by the coal at 950° C. and its susceptibility to the attack of pyridine. Also, whilst the retarding influence of oxygen upon the latter is again evident in B., it is far less marked than it was in the case of the Durham coal. Indeed, in the case of the Barnsley coal, the amount ultimately extracted in oxygen was a little more than that removed in nitrogen, even after allowance is made for the fact that the larger gross weight of the former is partly due to an absorption of oxygen, as the following analyses show :—

| | Percentage composition of extract. | | | | | Total carbon extracted per 100 coal. |
	C.	H.	N.	O. and S.	Ash.	
B. 3	81 ·98	5 ·92	1 ·50	10 ·43	0 ·17	9 ·5
B. 4 .... { (a) 79 ·69	5 ·97	1 ·48	12 ·21	0 ·65	} 10 ·3
(b) 75 ·37	3 ·82	1 ·50	18 ·74	0 ·57	

To discover the cause of the great difference between the behaviour of the two coals towards pyridine would probably require a much longer investigation than we have so far been able to make.

It may prove to be connected with another fact, discovered during the present enquiry, that the substance of coal B. apparently had a markedly stronger affinity for pyridine than that of coal A. Indeed, after the ether-washed "residues" had been kept *in vacuo* over sulphuric acid for 19 days they still retained pyridine with such tenacity that their weights always exceeded those of the original coal taken (*e.g.*, by 5·63 per cent. in B. 3 and no less than 9·47 per cent. in B. 4). This stronger affinity would seem to imply that the coal structure would be more easily "unbuilt" in the case of B. than in that of A., and, therefore, whatever proportion of really pyridine-soluble matter B. might contain would probably be more easily extracted, and the retarding influence of oxygen would be proportionately less marked than in the case of A.

It may here be mentioned that, in conformity with the foregoing supposition, the repeated disappearance and reappearance of colour during intermittent extraction, always observed in the coal A. (*q.v.*), was not noticed in the case of B. This again points to the structure of A. being more complex and

difficult to resolve than that of B., and it is possible that the much more pronounced coking properties of the former are attributable to this circumstance. These matters are, however, reserved for further investigation.

Part III.—THE ACTION OF PYRIDINE UPON "OXYGENATED" COALS A. AND B.

Seeing that the presence of oxygen has a retarding influence upon the solvent action of pyridine (more marked, however, in the case of coal A. than in that of B.), it seemed desirable to ascertain what would be the influence of "oxygenating" each coal beforehand, but excluding oxygen during the actual extraction.

Both of the coals in question absorb oxygen, forming "oxygenated" products, rather rapidly at temperatures above 80° and, as already stated, coal B. is, under such conditions, more readily oxidised than coal A. For the purposes of these experiments a sample of the "oxygenated" coal was prepared by circulating oxygen over about 90 grm. of the dried coals in question (previously ground to pass a 90-mesh sieve) at a temperature of 108° until between 10 and 11 litres of the gas had been absorbed. In such circumstances, although oxides of carbon and steam were evolved, the greater part of the oxygen remained in combination with the coal substance, producing "oxygenated" coals of the following percentage composition :—

	C.	H.	N.	S.	O.	Ash.
Oxygenated Coal A.	79·39	3·92	1·09	1·28	13·27	1·05
Oxygenated Coal B.	74·61	4·03	1·33	0·59	16·97	2·47

Ten grm. of each of these "oxygenated" coals were subsequently extracted with pyridine in the Soxhlet apparatus in an atmosphere of nitrogen, parallel experiments being also made simultaneously with the original coal in each case for purposes of comparison. The extractions were carried out (*a*) in the first instance for a period sufficient to remove the greater part of the extractable constituents, after which (*b*) the solvent was replaced by a fresh supply and the extraction continued for a further period until the "practical" limit had been well exceeded. The results in each case proved that "combined" is quite as potent as "free" oxygen in retarding the action of the solvent, as the following figures show :—

Coal A.

	Experiment A. 5 with original coal. (Percentage extracted.)	Experiment A. 6 with oxygenated coal. (Percentage extracted.)
Duration of Extraction Period—		
(a) 108 hours	23·90	12·53
(b) 120 ,, ...	1·73	3·53
Total...... 228 ,, ...	25·63	16·06

Coal B.

	Experiment B. 1. (Percentage extracted).	Experiment B. 2. (Percentage extracted.)
Duration of Extraction Period—		
(a) 128 hours	9·90	8·81
(b) 624 ,, ...	1·66	3·28
Total...... 752 ,, ...	11·56	12·09

Comparing now the results of A. 5 and A. 6 with those of A. 3 and A. 4 (recorded on p. 130), it will be seen that the "combined" oxygen in A. 6 retarded the extraction in almost the same degree as did the "free" oxygen in A. 4. The same also applies in the corresponding B. experiments, as a comparison between the results of B. 1(a) and B. 2(a) and those of B. 3(a) and B. 4(a) will show, although the retarding influence in the case of coal B. was so much less pronounced than in the case of coal A.

The further discussion of the bearing of the results recorded in this paper upon the chemistry of the coal substance is reserved for a further communication which will deal with some later developments of the investigation.